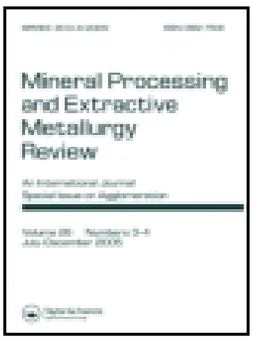

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Managing clay minerals in froth flotation—A critical review

Xumeng Chen and Yongjun Peng

School of Chemical Engineering, The University of Queensland, Brisbane, QLD, Australia

ABSTRACT

Clay minerals are widely present in various ore deposits as gangue minerals. The processing of high-clay-content ores is becoming a significant challenge for the mining industry owing to the poor flotation performance caused by the presence of clay minerals. Different types of clay minerals are typically present in ore bodies, and they cause several detrimental effects to flotation that require different treatments. In this article, a comprehensive review of the studies on understanding and mitigating the negative effects of clay minerals in flotation is presented. It starts with a review of the classification and structures of clay minerals commonly occurring in ore deposits and their properties that determine the behavior of clay minerals in flotation. It is followed by a critical review of two main negative effects of clay minerals on flotation, the recent research findings mainly from The University of Queensland group. The first negative effect is the coating of clay minerals on the surface of valuable minerals that decreases the floatability of valuable minerals. The second negative effect is the formation of network structures in the slurry. Depending on the type and strength of the network structure, it can cause either high pulp viscosity or increased gangue entrainment, which reduces the flotation recovery and flotation product grade, respectively. In this section, the mechanisms and key factors behind each negative effect are presented and critically discussed. Then, the approaches and techniques developed to mitigate the different negative effects of clay minerals are reviewed. To conclude, future directions for a more complete understanding of mechanisms and problem solving are recommended.

KEYWORDS

Clay minerals; flotation; slime coating; rheology; entrainment

Introduction

Clay minerals refer to a group of hydrous aluminum phyllosilicates that are fundamentally built of tetrahedral (T) sheets and octahedral (O) sheets (Brigatti et al. 2013). They are widely present in many ore deposits (e.g., base metal, precious metal, iron, and coal ore deposits) primarily as gangue minerals, and the ore deposits are typically characterized by the presence of different types of clay minerals (Ma et al. 2009; Tao et al. 2010; Wang et al. 2013; Zhang and Peng 2015a). With the inevitable depletion of high-grade ores, more and more low-grade and complex ores with high-clay contents should be processed. There is a common industrial observation that clay minerals are detrimental to flotation, including the generation of a low flotation recovery and/or low flotation product grade (Seaman et al. 2012; Wang and Peng 2013; Zhang 2016). There have been various mechanisms identified for the poor flotation performance in the presence of clay minerals. However, it is still difficult for the industry to clearly identify the main mechanism behind each case, and hence it is a challenge to develop suitable remedial strategies to improve the flotation performance.

Previous research studies and industrial observations have indicated that clay minerals normally have three negative effects on flotation. The first negative effect is the coating of clay minerals on valuable minerals, which prevents the adsorption of collectors on valuable minerals and reduces their floatability (Arnold and Aplan 1986a; Taggart et al. 1930; Arnold and Aplan 1986b; Attia and Deason 1989; Oats et al. 2010). The second negative effect is the increase in pulp viscosity in the presence of a certain type of clay mineral that can result in a significant reduction in flotation recovery (Bakker et al. 2010; Farrokhpay 2011; Ndlovu et al. 2011; Shabalala et al. 2011; Patra et al. 2012). The third negative effect is the high entrainment of clay minerals that significantly reduces the grade of flotation concentrates (Forrest et al. 1994; Akdemir and Sönmez 2003; Wang et al. 2015a).

In general, the most commonly occurring clay minerals in ore bodies can be classified into three groups: kaolin group, smectite group, and illite group, which have different effects on flotation (Cruz et al. 2013; Wang et al. 2015a, 2015b; Zhang and Peng 2015a; Cruz et al. 2015c). Kaolin group clay minerals typically cause significant gangue entrainment but only cause high viscosity at a high concentration. Smectite group clay minerals are the most problematic clay minerals in flotation owing to their ability to increase the pulp viscosity even at a low concentration. Illite group clay minerals have the least negative effect on flotation among the three types of clay minerals. Recent research findings at The University of Queensland showed that the negative effects of clay minerals on flotation are mainly relevant to the network structures formed (Cruz et al. 2015b; Zhang et al. 2015b, 2015c; Wang et al. 2016). It is therefore important to critically review these previous studies to understand the various effects of clay minerals on flotation and also identify the future work required for a more complete understanding of the mechanisms behind the problems.

CONTACT Yongjun Peng yongjun.peng@uq.edu.au School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

The ultimate purpose of studying the negative effects of clay minerals on flotation is to mitigate these negative effects. To remove the clay slime coating from valuable mineral surfaces, both physical and chemical pretreatments have been developed. The physical pretreatment includes the application of high intensity agitation, desliming hydrocyclone, and ultrasonic treatment (Celik et al. 2002; Oats et al. 2010; Yu et al. 2017a, 2017b). The chemical treatment is mainly the application of various dispersants (Seaman et al. 2012; Wei et al. 2013; Liu and Peng 2015). To reduce the pulp viscosity, most studies focused on applying either inorganic or polymeric dispersants to modify the clay network structures (Papo et al. 2002; Konan et al. 2008; Goh et al. 2011; Zhang et al. 2012). To reduce the entrainment of clay minerals, only a recent study proposed the application of polymers to selectively enlarge clay aggregates (Liu and Peng 2014). Although various approaches and techniques have been developed, their application on plant scales is still rare. The most common way to treat high-clay-content ores in flotation plants is to blend them at a small proportion with easier-to-process ores or process them at lower solid concentrations, which inevitably reduces the flotation productivity (Connelly, 2011; Peng and Zhao 2011; Quast et al. 2008; Zhang and Peng, 2015a).

In the following sections, a comprehensive review of flotation in the presence of clay minerals is presented. It starts with the review of structures and properties of clay minerals related to flotation, followed by a detailed review of the main negative effects of clay minerals on flotation and the mechanisms and key factors involved. The methods developed in the literature to mitigate the negative effects of clay minerals on flotation are also critically reviewed. Based on the literature review, future studies required for a more complete understanding of mechanisms and the development of more effective treatment methods are recommended.

Structures and properties of clay minerals

Classification and structures of clay minerals

Clay minerals are all fundamentally built of tetrahedral (T) sheets and octahedral (O) sheets that are bonded in certain proportions with various forces and atoms to form clay macrostructure (Brigatti et al. 2013). Based on the layer structures and bonding forces of layers, the most commonly occurring clay minerals in ore deposits can be classified into three groups: kaolin, smectite, and illite (Cruz 2016; Wang 2016; Zhang 2016). The structure representative of a mineral in each group is shown in Figure 1. Kaolinite has a 1:1 layer structure, and there are two types of forces holding the sheets together: van der Waals attractive forces, and hydrogen bonds between the hydrogen atoms of the hydroxyl groups in the octahedral sheet of one kaolinite layer and the oxygen atoms in the tetrahedral sheet of the next kaolinite layer. Water cannot penetrate between kaolinite layers owing to the strong hydrogen bonding between the layers, and therefore, kaolinite is generally non-swelling in water. Different from kaolinite, montmorillonite in the smectite group has a 2:1 layer structure. Moreover, there is no possibility of hydrogen bonding since both the outer sheets are tetrahedral meaning that there are no exposed hydroxyl groups at the surface. As a result, the montmorillonite sheets are loosely held together by weak van der Waals forces and can be separated by the penetration of water molecules, which leads to the swelling of montmorillonite producing a significant yield stress even at low concentrations. Illite has the same 2:1 layer as montmorillonite. However, illite layers are tightly bonded together by potassium ions that prevent the penetration of water into the structure. In consequence, the swelling potential of illite is low.

Based on studies at The University of Queensland, the different layer structures and bonding forces have significant influences on the properties of clay minerals, such as surface charge, ion exchange, and aggregation, and therefore result in different behaviors of clay minerals in flotation.

Charge properties of clay minerals in slurry

Electrical charges of minerals have significant effects on their surface reactivity, particle dispersion, and aggregation in aqueous suspensions and therefore play important roles in flotation. Figure 2 shows the zeta potential measurements of the three representative clay minerals. It can be observed that all the three clay minerals are negatively charged across the whole pH range. However, these zeta potential measurements show the overall potential of clay particles. Clay mineral crystallites display two graphically different surfaces: the basal face surface and the edge surface. These surfaces present quite different electrical charge properties. The aggregation of clay minerals and the electrostatic interaction between clay mineral and valuable minerals are

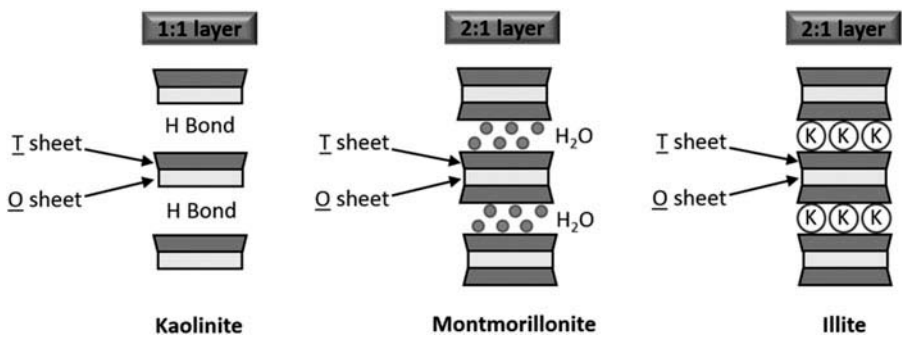

Figure 1. A schematic diagram of the structures of kaolinite, montmorillonite, and illite (Zhang 2016).

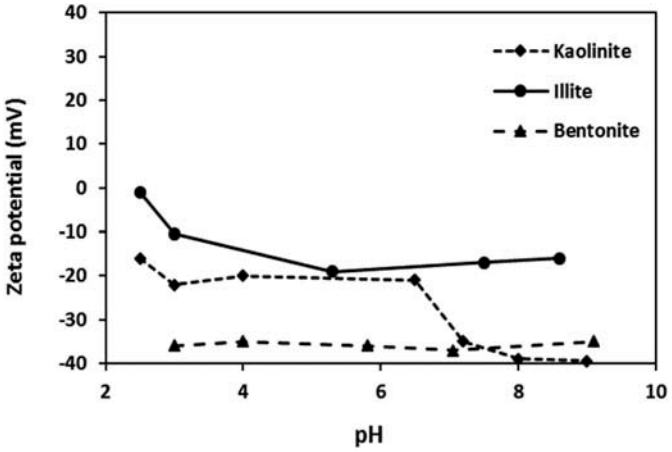

Figure 2. Zeta-potential of kaolinite, illite, and bentonite in DI water (Arnold and Aplan 1986b).

determined by the charges on basal faces or edges rather than the overall charge. Therefore, it is important to separately characterize the charges on basal surfaces and edge surfaces.

It is generally accepted that the basal surfaces of most clay minerals have permanently negative charges caused by isomorphous substitutions. For example, Si^{4+} in the tetrahedral sheet may be replaced by trivalent cations (Al^{3+} or Fe^{3+}), while Al^{3+} in the octahedral sheet may be replaced by divalent cations (Mg^{2+} or Fe^{2+}). Consequently, a charge deficiency occurs and a negative potential at the basal surface of the clay is created. Although this theory is widely accepted, a recent study by Gupta and Miller (2010) indicated that the two basal plane surfaces of kaolinite could carry positive or negative charges depending on pH. In that study, a colloidal force measurement showed that the silica tetrahedral face was negatively charged at pH > 4 and the alumina octahedral face was negative at pH > 8 but positive at pH < 6.

Different from the basal surfaces, the charge on the edges of clay minerals can be either positive or negative depending on the pH. The lattice of the crystallite is typically disrupted at the edges, and therefore a broken bond surface is exposed. Additional polar sites at the broken edges are mainly the octahedral Al–OH and tetrahedral Si–OH groups. These amphoteric sites are conditionally charged, and variable (either positive or negative) charges can develop at the edges by adsorbing hydrogen or hydroxyl ions from an aqueous phase in accordance with the pH (Tombácz and Szekeres, 2004).

The charge properties of clay minerals play important roles in clay–clay/clay–mineral interactions in aqueous suspensions. Therefore, different charge properties of different clay minerals and the change of surface charge with solution chemistry have a significant influence on the flotation behavior.

Effects of clay minerals on flotation

Clay minerals can cause different negative effects on flotation depending on the structures of clay minerals, the properties of valuable minerals, and the flotation conditions. The coating of clay minerals on valuable mineral surfaces and the formation of network structures in slurry are the two main mechanisms responsible for the negative effects. In the following sections, these two mechanisms and the related negative effects on flotation are reviewed separately.

Coatings of clay minerals and their effects on flotation

It has been widely observed that fine clay minerals can coat the surfaces of a range of valuable minerals and coals (Taggart et al. 1930; Giudice 1934; Arnold and Aplan 1986a; Arnold and Aplan 1986b; Attia and Deason 1989; Xu et al. 2003; Oats et al. 2010; Wang et al. 2013; Forbes et al. 2014; Chen et al. 2017b, Yu et al. 2017a). As most clay minerals are highly hydrophilic, the coating of clay minerals on valuable mineral surfaces can then prevent the adsorption of collectors on valuable minerals and reduce their surface hydrophobicity, which not only depresses the mineral flotation but also reduces the concentrate grade (Gaudin et al. 1960; Edwards et al. 1980; Bremmell et al. 2005). Owing to the fine particle size of clay minerals, the coating of clay minerals is typically termed "slime coating." However, it should be clarified that slime coating also includes the coating by other fine minerals other than clay minerals. For any coating to occur, there must be attraction forces existing between clay minerals and valuable minerals. Most of previous studies attributed electrostatic force to be the main force controlling clay coating (Gaudin et al. 1960; Xu et al. 2003; Peng and Zhao 2011; Zhao and Peng 2012; Forbes et al. 2014). In addition, other mechanisms were also proposed to explain the clay coating (He et al. 2009; Oats et al. 2010; Uribe et al. 2016). These mechanisms and the main determining factors in flotation systems are critically reviewed in the following sections.

Clay slime coatings by electrostatic attraction and their effects on flotation

Based on the electrostatic attraction theory, the coating only occurs when the clay mineral and the valuable mineral carry opposite charges. As an example, Gaudin et al. (1960) showed that galena flotation at neutral conditions was not affected by kaolinite because both galena particles and kaolinite particles were negatively charged. In contrast, some positively charged slimes depressed galena flotation almost completely.

Different from most minerals, a clay mineral can carry different charges on basal faces and edges at the same time. As discussed in previous section, the basal face of clay minerals is normally negatively charged. However, the edge can become positively charged at pHs below its iso-electrical point (IEP). Although most of un-oxidized sulfide minerals or coals are negatively charged under normal flotation conditions, the clay coating can still occur through electrostatic attraction between negatively charged mineral/coal particles and positively charged edges of clay particles. Some researchers also state that slime coating is possible when the zeta potential values of both particles are low (Xu et al. 2003).

Effects of surface properties of valuable minerals on clay coatings. Un-oxidized sulfide minerals are negatively charged under normal flotation conditions; However, they become positively charged owing to surface oxidation during grinding and flotation. As shown in Figure 3(a), Peng and Zhao (2011)

found that chalcocite flotation was significantly depressed by the presence of bentonite, while the flotation of chalcopyrite was not affected. Figure 3(b) shows the zeta-potential measurements, which revealed that chalcocite became positively charged at pH 9 after grinding and electrostatically attractive to negatively charged bentonite, resulting in bentonite slime coatings on chalcocite surfaces. In contrast, chalcopyrite still remained negatively charged after grinding and thus its flotation was less affected by bentonite owing to the electrostatic repulsion between the two minerals. The different electrostatic properties between the two types of copper minerals were mainly caused by their different surface oxidation behaviors during grinding. X-ray photoelectron spectroscopy (XPS) analyses showed that chalcocite was heavily oxidized during grinding, and the presence of oxidation species altered the surface charges to positive. However, chalcopyrite was only slightly oxidized and therefore the surface was still negatively charged (Zhao and Peng 2012). Grinding of chalcocite under reducing conditions could mitigate bentonite slime coating owing to electrostatic repulsion between un-oxidized chalcocite and bentonite, which further supported the proposed mechanism. Later studies by the same authors determined that kaolinite could also coat the oxidized chalcocite surface through the same mechanism, corresponding to poor chalcocite flotation in the presence of kaolinite (Zhao and Peng 2014). These studies well explain the reason why inconsistent effects of clay minerals are typically observed when flotation plants process different types of copper ores.

In addition to sulfide minerals, the properties of coal particles also have significant effects on clay coatings. Arnold and Aplan (1986a) reported that the flotation of a low rank coal was more strongly affected by the presence of clay minerals than the flotation of a high rank coal. A similar finding was also reported by Quast et al. (2008) who demonstrated that the adverse effect of clay minerals on coal flotation was more pronounced for a moderately floating coal than a strongly floating coal. However, there was no direct evidence to show that the surfaces of lower rank coals were more attractive to the clay particles. It is possible that the flotation of lower rank coals is more sensitive to the surface coating owing to hydrogen bonding between hydrophilic coal surfaces and clay particles. Similar to different coal ranks, different oxidation levels of coal surfaces may also affect the slime coating. This is because oxidation can dramatically change the coal surface hydrophobicity, surface functional groups, and surface charge properties. It has been found that coal oxidation products such as humic acid can interact with clay slimes and more significantly reduce coal flotation at low pH values (Firth and Nicol 1981; Arnold and Aplan 1986b). However, this was attributed by Firth and Nicol (1981) to the increased affinity of clay particles for oily collectors. There is no study so far on whether the presence of oxidation groups on coal surfaces can affect the interaction between coal particles and clay minerals.

Effects of pH on clay coatings in flotation. The zeta potential of both clay minerals and coal particles is strongly dependent on pH, and therefore the change of pH will significantly change the electrostatic interaction. It is generally accepted that the basal surfaces of most clay minerals have permanently negative charges caused by isomorphous substitutions. Different from the basal surfaces, the charge on the edges of clay minerals can be either positive or negative depending on the pH. Theoretically, at high pH values, the clay edges and faces and the coal particles are all negatively charged and electrostatic attraction between them is not expected. At pH values below the IEP of minerals, the positively charged mineral surfaces should attract the negatively charged clay faces. At pH values below the IEP of the clay edges but above the IEP of minerals, slime coating can also occur between the positively charged clay edges and negatively charged mineral surfaces. Arnold and Aplan (1986b) studied the effect of pH on the slime coating of kaolinite and bentonite on three different coal samples. It was found that coal flotation was not depressed by clay minerals at pH 9; however, a significant depression was observed at pH 3.5 or even pH 6.5. Xu et al. (2003) also reported that the coating of montmorillonite on coals was less severe at pH 10 compared to that at pH 5. A recent study by Chen et al. (2017a) found that the slime coating of montmorillonite on coarse galena particles was more significant at acidic pH owing to less electrostatic repulsion between galena and montmorillonite, which confirmed the dominant role of electrostatic attraction in slime coatings.

Effects of electrolytes on clay coatings. A study by Zhao and Peng (2014) revealed that the presence of electrolytes in mineral suspensions had a significant effect on clay slime coatings. Kaolinite significantly depressed chalcocite flotation

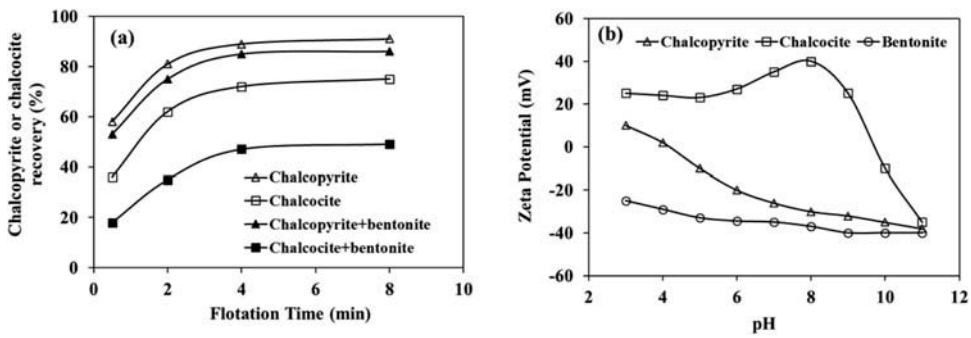

Figure 3. Chalcopyrite or chalcocite recovery as a function of flotation time in the presence and absence of bentonite (a) and zeta potentials of the three minerals (b) (Peng and Zhao 2011).

owing to slime coatings in fresh tap water; however, the recovery of chalcocite increased with an increase in electrolyte concentration. It was concluded that the electrolytes reduced the electrostatic attraction between kaolinite and chalcocite so that the surface coating of kaolinite on chalcocite surfaces was mitigated, leading to improved chalcocite flotation. In another recent study by Zhao et al. (2017), electrochemical impedance spectroscopy (EIS) was used for the first time to investigate clay coatings and the effects of electrolytes on mitigating clay coatings. It was found that the formation of kaolinite coatings on chalcocite surfaces decreased the dielectric constant and increased the impedance of chalcocite. Therefore, a reduction in impedance of a clay-coated mineral surface reflected the mitigation of the slime coating. As shown in Figure 4, impedance was lower in saline water than in deionized (DI) water, indicating that the electrolyte mitigated slime coatings. For the cations (Li^+, Na^+, and K^+) and anions (F^-, Cl^-, and I^-) examined in this study, the higher mw ions reduced the slime coating more than the lower mw ions presumably owing to the greater decrease of electrostatic attraction between chalcocite and kaolinite.

In coal flotation, the presence of various ions in water, such as Ca^{2+} and Mg^{2+}, can also have a significant effect on slime coatings. Arnold and Aplan (1986b) found that the use of tap water or the addition of Ca^{2+} or Mg^{2+} to DI water significantly improved the recovery of coal flotation that was depressed by clay minerals when DI water was used. It was proposed that the ions mitigated the effect of the charge on clay particles to prevent the formation of electrostatic slime coatings. However, no direct evidence of the mitigation of slime coating by ions was provided. It is possible that the ions improved the coal floatability through other mechanisms such as reduced bubble size, more stable froth, and reduced hydration of coal surfaces. In contrast, a recent study by Xing et al. (2016) showed that the coal–kaolinite hetero-coagulation occurred only after the Ca^{2+} concentration reached a certain level. Atomic force microscopy (AFM) measurements showed that the interaction forces between coal and kaolinite changed from weak repulsive to strong attractive and increased steadily with an increase in Ca^{2+} concentration. In this study, the increase of Ca^{2+} concentration only slightly decreased coal floatability but resulted in a sharp increase in product ash, which was attributed to kaolinite coating. However, it has been reported that the presence of salt ions can also increase the product ash through mechanical entrainment and entrapment of fine clay particles (Wang and Peng 2013; Wang et al. 2014a). Therefore, it is important to distinguish the effect of entrainment and entrapment from the effect of slime coatings when clay minerals and salts coexist in the system.

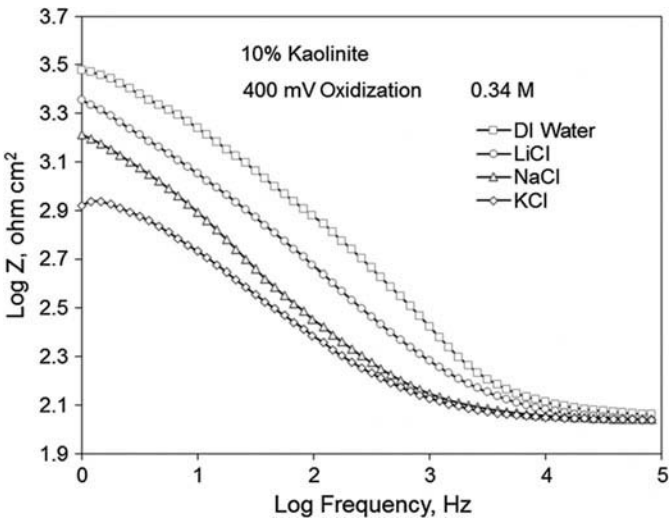

Figure 4. EIS (Bode plots) of chalcocite pre-oxidized at 400 mV in the presence of 10% kaolinite in deionized water, 0.34 M LiCl, 0.34 M NaCl, and 0.34 M KCl solutions (Zhao et al. 2017).

Clay slime coatings by other mechanisms and their effects on flotation

In addition to electrostatic attraction forces, some other mechanisms have been proposed to explain the clay coating. He et al. (2009) observed the coating of sericite on chalcocite surfaces when the zeta-potential of both chalcocite and sericite in the system was negative. As a result, the coating that occurred between the two negatively charged minerals was described as "unexpected" by the authors. However, they attributed this behavior to the production of Cu (II) ion complexes during the surface oxidation of chalcocite. Several possible mechanisms were proposed, including electrostatic-charge patch attraction, van der Waals attraction, adsorbed ion–particle bridging, surface nucleation, and cementation (He et al. 2009).

Derjaguin–Lan-dau–Verwey–Overbeek (DLVO) theory has been used in several studies to explain the coating of clay minerals on coal particles (Honaker et al. 2005; Oats et al. 2010; Gui et al. 2016; Yu et al. 2017a). Oats et al. (2010) calculated the interaction forces between clay minerals and coal particles based on the colloid stability theory and claimed that clay coatings on coal surfaces were governed by van der Waals attraction and that the double layer interaction played a secondary role. However, this calculation was based on some assumptions that may not represent the conditions in a real flotation system. A recent study by Yu et al. (2017a) proposed that van der Waals attraction became sufficiently strong to overcome the double-layer repulsion when kaolinite particles and coal particles came sufficiently close to each other. The authors also determined that mild agitation reduced the coal combustible recovery, and it was explained that mild agitation increased slime coatings by providing external energy to overcome the energy barrier for coal–kaolinite particle collision. However, more direct evidences are required to fully support the proposed mechanisms because the depressing effects of clay minerals on flotation can be caused by many other factors in addition to slime coatings. Moreover, it is important to isolate these different factors. Furthermore, a reliable characterization of slime coatings is also critical, but it is still a significant challenge in flotation systems.

A recent study by Uribe et al. (2016) reported that both kaolinite and smectite depressed chalcopyrite flotation through slime coatings although the surface of chalcopyrite at alkaline pH is always negatively charged even after strong oxidation (Fullston et al. 1999). One possible mechanism the authors proposed was the hetero-coagulation between

chalcopyrite and clay minerals caused by Ca^{2+} from lime that was added to the process to adjust pH. The slime coating was confirmed by measuring the change in turbidity in the clay particle suspensions after adding copper minerals. In addition to slime coating, the authors also observed that clay particles coated bubble surfaces, which affected the adhesion between chalcopyrite particles and bubbles. This study suggests that it is important to consider the potential effects of ions introduced from pH modifiers or process water on slime coating.

In general, previous studies have shown that slime coating by clay minerals can occur in flotation systems, and it depends on the type of clay minerals, the properties of mineral/coal particles, the pH of particle suspensions, and the concentration of ions in water.

Formation of clay network structures and their effects on flotation

Formation of clay network structures

Clay minerals are considered as colloidal materials with an upper particle size between 1 μm and 4 μm. In an ideal aqueous dispersion, individual layers of clay minerals are randomly oriented and are constantly moving. In real mineral suspensions, depending on the properties of clay minerals, shear stress, and the solution chemistry, clay minerals can be present as single layers, particles, or aggregates. As shown in Figure 5, when aggregated, three different modes of particle association may occur: face-to-face (F–F), edge-to-face (E–F), and edge-to-edge (E–E) (van Olphen, 1977). They are governed by the state of balance between van der Waals attraction and electrostatic forces that exist between charged double layers at the surfaces of clay platelets with the latter being either attractive or repulsive depending on the charge of the surfaces. The face-to-face (F–F) network may form three-dimensional structures when the free energy of the system is at its lowest level (Rand and Melton, 1977). The house-of-cards (E–F) network only forms when the edges are positively charged, or in a slightly alkaline medium above the critical salt concentration owing to the electrostatic attraction between edges and faces (Lagaly, 2006). The edge-to-edge (E–E) contact may occur under conditions of low ionic strength at the pH value close to the IEP of the edge surface of clay particles (Rand and Melton, 1977).

Effects of clay network structures on flotation through the modification of pulp rheology

The dispersion/aggregation state of clay minerals has a significant effect on pulp rheology. At low concentrations, no aggregates form and the clay suspensions often exhibit Newtonian behavior. With the increase of solids concentration, small aggregates will start to form, and pulp viscosity increases accordingly. The extent and complexity of rheology modified by clay minerals are mainly determined by the type of network structures formed in mineral suspensions. In general, E–F and E–E network structures are characterized by non-Newtonian flow with the development of yield stress and produce a high viscosity in suspensions (Ndlovu et al. 2011). In contrast, the formation of F–F structure decreases the gel strength with a lower yield stress because it reduces the number of units available to build gel structures and the surface available for particle interactions.

The modification of pulp rheology has significant effects on flotation. It has been found that an increase in rheological properties of flotation pulp significantly affects the hydrodynamics within flotation cells and therefore leads to the change of various flotation subprocesses including reduced gas dispersion and gas hold-up, decreased mobility of particles and bubbles, and reduced particle–bubble collision and attachment (Bakker et al. 2010; Shabalala et al. 2011). In addition, the change in pulp rheology can also significantly affect froth stability and froth texture as reviewed by Farrokhpay (2011). A number of recent studies have reported a strong relationship between flotation performance and pulp rheology. In most cases, an increase in pulp viscosity impedes the flotation kinetics with higher reagent consumption, lower recovery, and poorer selectivity (Patra et al. 2012; Wang et al. 2015b, Zhang and Peng 2015a; Chen et al. 2017c). However, some studies have demonstrated that the recovery of coarse particles and particles with high specific gravity (e.g., gold) can benefit from a slight increase in pulp viscosity owing to the formation of more stable bubble–particle aggregates (Xu et al. 2012a, Zhang and Peng 2015a).

Effects of clay mineral type. In mineral flotation, there are many factors that can affect the formation of clay network structures and then affect pulp rheology and flotation performance. The most important factor is the type of clay minerals. Owing to different compositions, structures, and charge properties, different clay minerals form different network structures and affect pulp rheology quite differently. Ndlovu et al. (2014) compared the rheological properties of suspensions of common clay minerals. The critical concentration was calculated, beyond which exponential increments in the suspension yield stress and viscosity were observed. This is also typically the concentration at which rheological problems start to affect mineral flotation. It has been found that montmorillonite

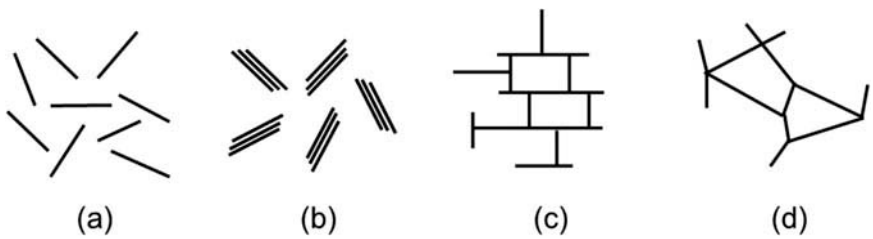

Figure 5. Modes of particle associations in clay suspensions: (a) dispersed, (b) F–F, (c) E–F, (d) E–E (Luckham and Rossi 1999).

results in suspensions with complex rheology at critical concentration as low as 4% solids by volume, kaolinite suspensions only become problematic at concentrations higher than 10% solids by volume, and illite and muscovite suspensions do not show yield stress even at 30% solids concentration by volume. Although the platy clay minerals have a relatively high critical concentration, it is lower than that of quartz, demonstrating the rheological complexity of clay minerals relative to non-clay minerals. Recent studies at The University of Queensland have applied Cryo-scanning electron microscopy (Cryo-SEM) to directly characterize the network structure formed under real flotation conditions (Cruz et al. 2015c). Figure 6 shows the type of aggregates and network structures present in the pulp of copper/gold ore–bentonite and copper/gold ore–kaolinite mixtures. It is clear that there are differences in kaolinite and bentonite particle aggregates. Bentonite created a honeycomb-like network structure that appeared to be made of many interconnected cells with the pore size at approximately 5–10 μm in diameter and E–E and E–F aggregates being predominant. Kaolinite platelets associated mainly in the mode of F–F and E–E as dense elongated strings and the resulting aggregates were joined to each other commonly in an E–F manner to form loose clumps. No honeycomb-like network structure was observed in the pulp of ore–kaolinite mixtures.

In addition to the type of clay mineral, its degree of crystallinity also plays an important role in the rheological behavior of clay mineral suspensions. For example, Zhang and Peng (2015a) reported that poorly crystalline kaolinite, Q38, produced higher apparent viscosity and yield stress than the well crystalline kaolinite, snobrite. Poorly crystalline clay minerals are composed of thinner plates, and therefore more individual edges and corners are available to initiate friction during shearing, resulting in higher yield stress and viscosity (Murray and Lyons 1959). In addition, Du et al. (2010) reported that complex surface morphology of poorly crystalline clay minerals resisted the transformation of loose E–F structures to dense F–F structures under shear that can also lead to higher apparent viscosity. These studies indicate that the degree of crystallinity should also be considered in addition to the type of clay minerals when investigating the pulp rheology in mineral flotation.

The rheological behavior of different clay minerals is generally consistent with their effects on mineral flotation recovery (Patra et al. 2012; Zhang and Peng 2015a). A recent study conducted by Zhang and Peng (2015a) investigated the flotation of a copper/gold ore in the presence of snorbite, Q38, and bentonite. As shown in Figure 7, with an increase in clay content, copper flotation was more significantly depressed in the presence of bentonite than in the presence of kaolinite and the change in flotation recovery was well correlated with the change of apparent viscosity. The roles of kaolinite and bentonite in copper flotation were further determined in a later study by Wang et al. (2015b) who confirmed that bentonite was more problematic than kaolinite in terms of modifying the pulp viscosity during flotation. Another recent study by Basnayaka et al. (2017) reported that the presence of bentonite modified the pulp rheology and reduced the flotation recovery of gold more significantly than kaolinite. In mineral processing plants, various types of clay minerals can be present in a typical ore sample, and therefore it is important to understand the rheological behavior of each type of clay minerals and the effects on the flotation process.

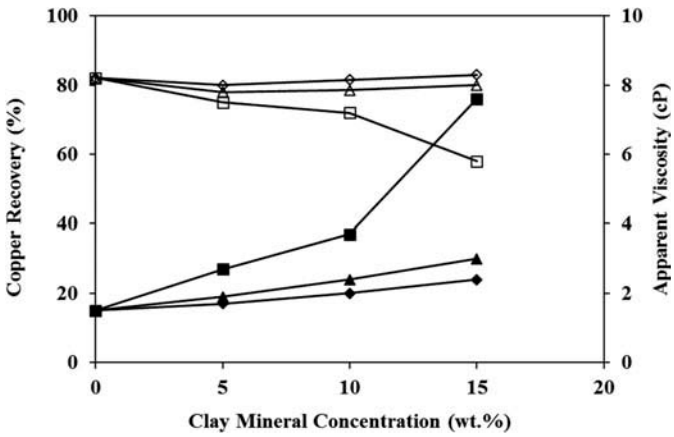

Figure 7. Effect of clay minerals on copper recovery (hollow points) and apparent viscosity (solid points) of flotation slurries: snobrite (♦), Q38 (▲), bentonite (■) (Zhang and Peng 2015a).

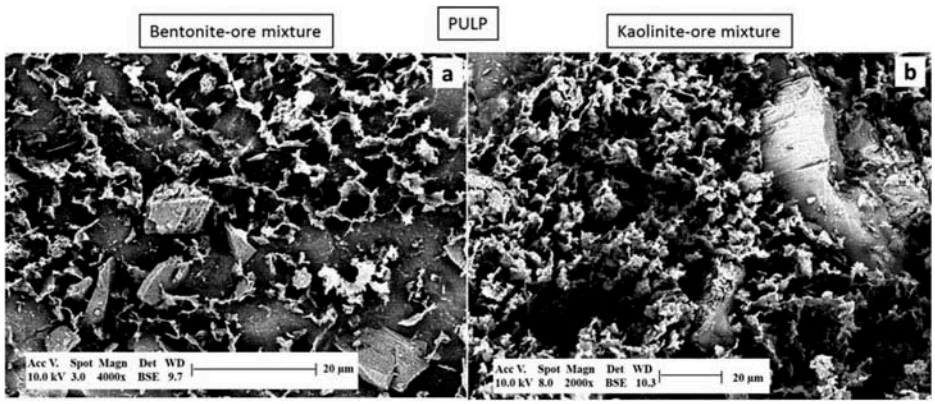

Figure 6. Comparison of the sodium bentonite network structures and kaolinite aggregates in the clay-ore mixtures: sodium bentonite and kaolinite concentrations are 15 wt.% and 30 wt.%, respectively; 4000× magnification (Cruz et al. 2015c).

Effects of pH. In flotation plants, pH is carefully controlled to facilitate the flotation of valuable minerals and the depression of unwanted gangue minerals. When clay minerals are present in the ore samples, the pH can have a significant effect on the slurry viscosity owing to the change of clay network structures. Taking kaolinite as an example, as shown in Figure 8, when pH is below the IEP of the edge surface of clay particles, the edge is positively charged and the basal surface is negatively charged, as a result, the house-of-cards (E–F) network can form owing to the electrostatic attraction between edges and faces. This network is typically characterized by a non-Newtonian flow with the presence of yield stress. E–E association is expected in the pH region around the IEP of the edge as a result of the minimum repulsion between the edges, and this type of structure typically has less rheological complexity. When pH is higher than the IEP of the edge with both the edges and basal surfaces of a kaolinite particle being negatively charged, the clay particles will be dispersed owing to strong repulsive forces between the particles.

Similar to kaolinite dispersions, bentonite dispersions also exhibit higher yield stress at low pH values owing to the formation of house-of-cards networks. With increasing pH, the number of E–F linkages decreased owing to the reduction of positive charge on the edges, leading to breakup of the house-of-cards networks and a sharp decrease in yield stress. After reaching the minimum yield stress, the further increase of pH will gradually increase the yield stress. This is attributed to the delamination at high pH, which reduces the clay aggregate size and increases the specific surface area (Permien and Lagaly, 1995; Goh et al., 2011). Increasing the pH above 7 by adding NaOH reduces the degree of delamination and the electroviscous effect, resulting again in a decrease in shear stress (Lagaly, 2006).

In general, pH can have a significant effect on the rheological behavior of clay minerals and should be considered when adjusting the pH of a flotation slurry with a high content of clay minerals. In addition, it may be also beneficial to reduce the viscosity of flotation pulp by adjusting the pH if the floatability of valuable minerals and other gangue minerals will not be negatively affected. However, no such study has been reported so far.

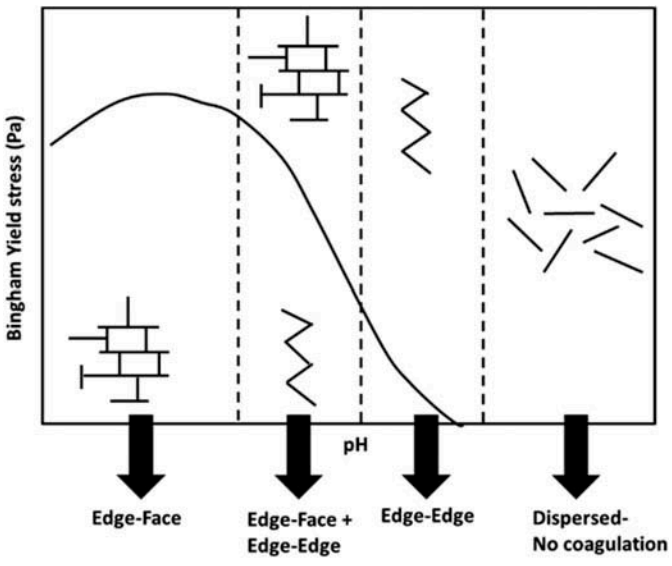

Figure 8. Interpretation of the effect of pH on the Bingham yield stress of kaolinite suspensions in terms of the mode of particle interactions (Ndlovu et al. 2011).

Effects of electrolytes. In mineral flotation, various ions are present in the slurry, such as Ca^{2+}, Na^{+}, Mg^{2+} cations and Cl^{-}, SO_4^{2-}, CO_3^{2-} anions. These ions can significantly modify the network structure of clay aggregates and therefore change the rheology of particle suspensions. For example, the addition of salts (e.g., NaCl and $CaCl_2$) can result in a significant decrease in viscosity of montmorillonite suspensions (Heller and Keren 2001; Lagaly and Ziesmer 2003; Suzuki et al. 2005). Several mechanisms have been proposed to explain the roles of salts, including the reduction of the thickness of the diffuse ionic layer, the disruption of network structures and the formation of more particle-like aggregates. In mineral processing, most salt ions are introduced through the addition of pH modifiers (e.g., lime, soda ash), the presence of soluble gangue minerals (e.g., gypsum, calcite), and the use of high salinity water or seawater in the plant.

Cruz et al. (2013) investigated the effect of pH modifiers including lime, sodium hydroxide, and soda ash on the rheology of clay minerals. They found that the pH modifier had little effect on the rheological properties of kaolinite and bentonite suspensions at low solid concentrations (10 wt.% kaolinite and 2 wt.% bentonite) but significantly altered the rheological properties of suspensions at high solids concentrations (20 and 30 wt.% kaolinite and 5 and 10 wt.% bentonite). As shown in Figure 9, NaOH had little effect on the rheology of a 30% kaolinite suspension, lime increased the pulp viscosity and Na_2CO_3 reduced the pulp viscosity. In contrast, Figure 10 shows that Na_2CO_3 acted as an aggregator instead of a dispersant in bentonite suspensions enhancing the aggregation even more than lime, and NaOH also induced aggregation in bentonite suspensions. A later study by the same authors further investigated the effect of lime and soda ash as pH modifiers on the flotation of a copper–gold ore mixed with kaolinite (Cruz et al. 2015b). Although rheology measurements showed that, at the same pH values, lime increased apparent viscosity more than soda ash, Cryo-SEM analyses of all the flotation samples indicated that the kaolinite aggregates in the slurry were similar in structure for both lime and soda ash additions. These findings suggest that Ca^{2+} ions released from lime did not alter the clay network structure but led to the formation of stronger aggregates. Flotation results showed that the application of lime did not have a significant effect on copper/gold recovery but reduced the product grade owing to the increased mass recovery that was related to the formation of stronger aggregates.

Some gangue minerals present in ores are partially soluble and can release ions into water during processing. Cruz et al. (2015a) investigated the interaction between clay minerals and major calcium-bearing gangue minerals using rheological measurements. Gypsum was found to have the highest solubility in water and released the largest quantity of Ca^{2+} ions resulting in a significant interaction with illite and kaolinite, enhancing their rheological properties. Calcite and dolomite were found to be less

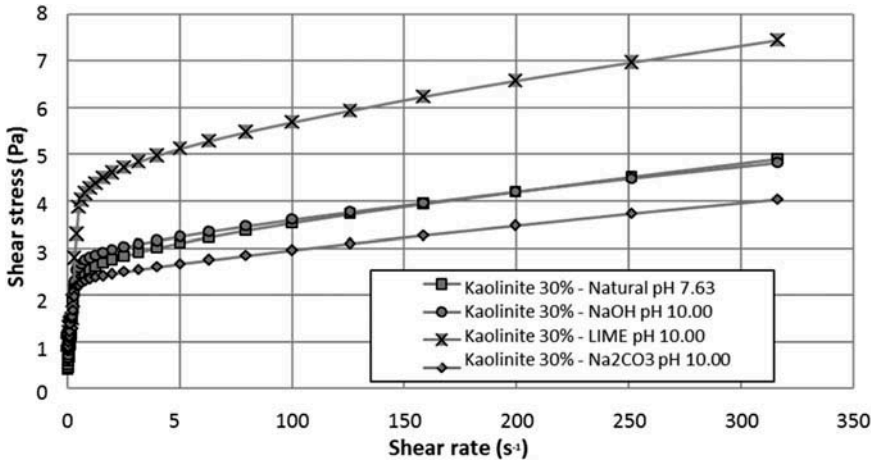

Figure 9. Rheograms of 30 wt.% kaolinite suspensions in the absence and presence of pH modifiers (Cruz et al. 2013).

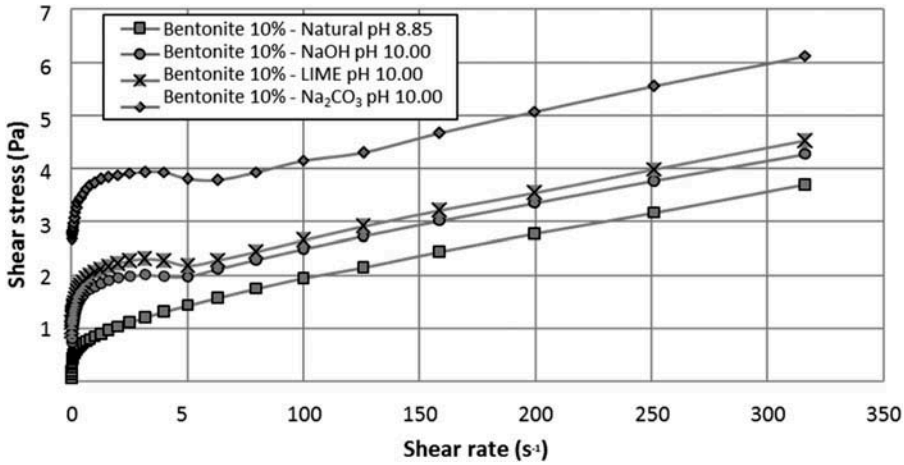

Figure 10. Rheograms of 10 wt.% bentonite suspensions in the absence and presence of pH modifiers (Cruz et al. 2013).

soluble and exhibited a lower interaction with these clay minerals. This study also investigated the interaction of the three calcium-bearing minerals with bentonite, a swelling clay mineral. Gypsum had the greatest interaction with bentonite but affected the rheological characteristics of bentonite in the opposite way to that observed with illite and kaolinite. Ca^{2+} ions released from gypsum dispersed bentonite slurries by preventing the swelling of this clay mineral, reducing the slurry viscosity. In a later study by the authors, the effect of gypsum on the flotation of a copper-gold ore in the presence of clay minerals was investigated (Cruz et al. 2015c). As shown in Figure 11, the presence of 15% bentonite significantly decreased copper flotation recovery; however, the addition of 5% gypsum almost completely restored the copper recovery mainly due to the decrease of pulp viscosity. The change of aggregation structure was monitored by Cyro-SEM. As shown in Figure 12, bentonite created a honeycomb-like network structure that was made of many interconnected cells with a pore size of approximately 5–10 μm in diameter and E–E and E–F aggregates being predominant. When gypsum was added to the bentonite-ore mixture, the extensive E–E-connected long strings formed without any E–F associations and the bentonite aggregates were thicker owing to more F–F associations as compared to the bentonite-ore mixture. The effect of gypsum on rheology and flotation was even more noticeable than the effect of pH modifiers because gypsum released sufficient quantities of Ca^{2+} ions. A recent study by Basnayaka et al. (2017) confirmed that the addition of Ca^{2+} reduced the adverse effects of bentonite on flotation by modifying the swelling properties of bentonite and then reducing the pulp viscosity. These studies suggest that when investigating ores with clay minerals, it is important to consider the potential input from other gangue minerals on the interactions in determining the rheological behavior.

Zhang et al. (2015b) investigated the flotation of a copper–gold ore in the presence of 10% bentonite in tap water and sea water. It was found that bentonite had a deleterious effect on copper and gold flotation in tap water, but this deleterious effect was mitigated in sea water. The different flotation behavior in tap water and sea water was caused by a change of pulp viscosity. As shown in Figure 13, the addition of 10% bentonite into the clean ore significantly increased the pulp viscosity, which was responsible for the deteriorated flotation performance; however, the application of sea water clearly reduced pulp viscosity and therefore improved flotation. The characterization of network structures by Cryo-SEM revealed that sea water reduced the swelling capacity of bentonite and modified the association modes of bentonite platelets in flotation pulp, resulting in the breakup of links between the

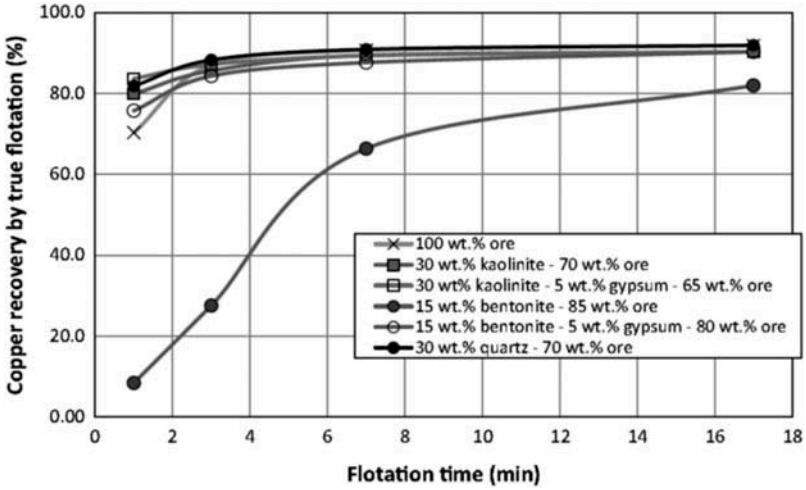

Figure 11. Copper recovery by true flotation from the flotation of the ore and its mixtures with quartz, clay minerals, and gypsum (Cruz et al. 2015c).

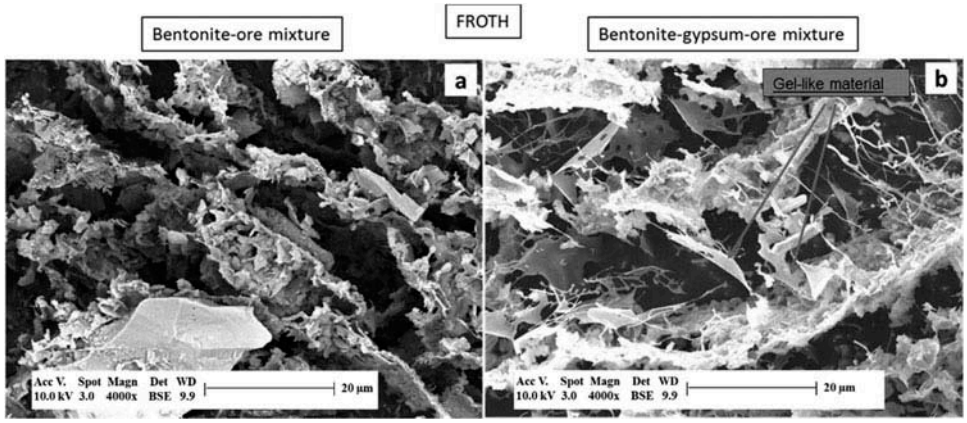

Figure 12. Cryo-SEM images illustrating the change in froth agglomerates from the ore–bentonite mixture (a) to the ore–bentonite–gypsum mixture (b): 4000× magnification (Cruz et al. 2015c)).

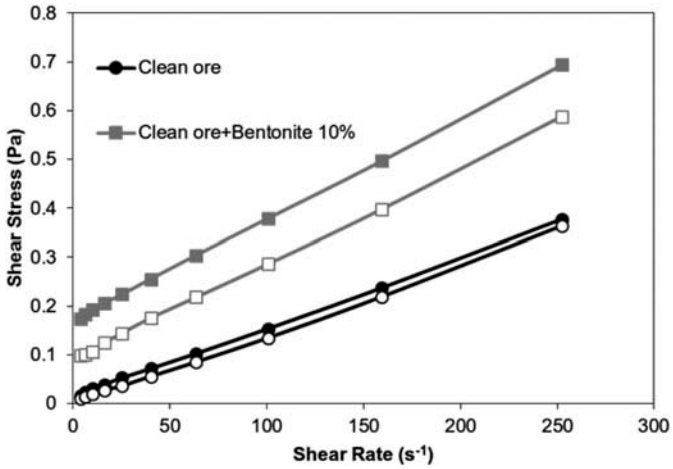

Figure 13. Rheograms of clean ore slurries in the absence and presence of bentonite in tap (solid points) and sea water (hollow points) (Zhang et al. 2015b).

structures with relatively large pores. A further study by Wang et al. (2016) investigated the effect of different cations, Na^+, K^+, Mg^{2+}, and Ca^{2+} with the same anion, Cl^-, on the rheology of a copper--gold ore in the presence of bentonite and copper flotation. It was determined that the improvement of copper flotation in the presence of bentonite was generally dependent on the reduction of pulp viscosity by these cations. Divalent cations, Mg^{2+} and Ca^{2+}, had a more significant effect on pulp viscosity and therefore copper flotation than monovalent cations, Na^+ and K^+.

Effects of clay network structures on entrainment

Another adverse effect of clay minerals on mineral flotation is the dilution of concentrate grade caused by clay minerals entering the froth through mechanical entrainment. Entrainment is a mechanical mass transfer process where particles suspended in water between bubbles enter the flotation froth from the top of pulp region and are transferred to the concentrate (Gaudin 1957; Bisshop and White 1976; Wang et al. 2015a). In mineral flotation, entrainment occurs simultaneously along with true flotation and is a primary mechanism for the recovery of fine gangue particles. Different from true flotation, which is chemically selective to mineral surface properties, entrainment is a nonselective process. Several factors including water recovery, pulp density,

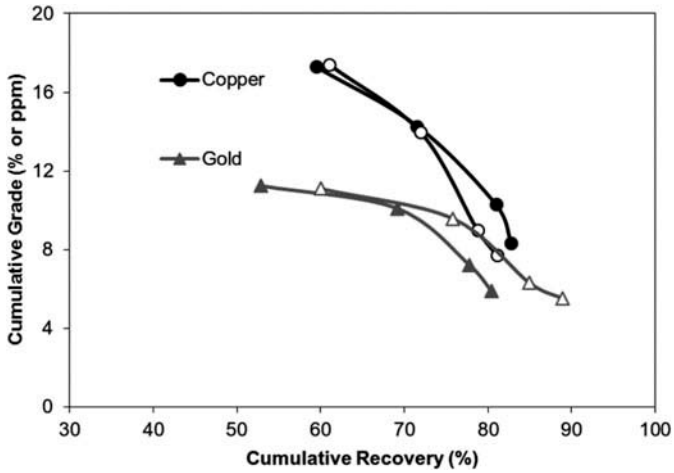

Figure 14. Cumulative copper or gold grade as a function of the cumulative copper or gold recovery in the flotation of clean ore mixed with 15 wt.% quartz (solid points) or kaolinite (hollow points) (Zhang et al. 2015c).

particle size, particle density, gas flow rate, rheology, and froth structure can affect entrainment (Savassi et al. 1998, Wang et al. 2015a). It was traditionally believed that the high entrainment of clay minerals was related to their fine particle size. The degree of entrainment increases with decreasing particle size, and mechanical entrainment is significant for particles under 30 μm (Smith and Warren 1989). Coarse particles drain more readily from the voids between the bubbles than fine particles. The size of most clay minerals is considerably smaller than 30 μm, and it is common to find clay particles of less than 2 μm in the flotation of coals and base metal minerals regardless of the grinding procedures (Tu et al., 2005; Liu and Peng 2014). Given this small size of clay minerals in ores, it is highly likely that they will be transported to the froth via entrainment and have a negative effect on the concentrate grade. However, in addition to the fine particle size, recent studies at The University of Queensland showed that the aggregation structures of clay minerals in the pulp play a critical role in the degree of entrainment (Cruz et al. 2015b, 2015c; Zhang et al. 2015c).

Zhang et al. (2015c) demonstrated that the presence of kaolinite had a negative effect on copper and gold flotation product grades. As shown in Figure 14, both copper and gold grade were significantly lower in the flotation of a clean ore mixed with 15 wt.% kaolinite compared to the flotation of the same ore with 15 wt.% quartz that had the same size distribution with kaolinite. The low product grade was mainly caused by kaolinite platelets reporting together with their aggregates from the pulp to the froth through entrainment. The high entrainment of kaolinite particles was closely correlated with the formation of loose network structures with low density. Compared to kaolinite, bentonite and illite had a less effect on the concentrate grade owing to a lower degree of entrainment (Zhang and Peng 2015a; Zhang et al. 2015b; Zhang 2016). Bentonite significantly reduced the flotation recovery owing to high viscosity, and thus the effect on entrainment became insignificant. Illite was also less problematic than kaolinite in reducing copper/gold grade, which was due to its lack of E–F contacts to build up porous network structures. This finding strongly supports that the structure and property of a specific type of clay mineral are critical in determining entrainment in mineral flotation.

In addition to different types of clay minerals, the modification of clay network structures by the presence of electrolytes also affects entrainment. It has been found that the negative effect of kaolinite was exaggerated when sea water was used as evidenced by the increased kaolinite recovery with a further reduction in concentrate grade (Zhang et al. 2015c). As shown in Figure 15, while kaolinite platelets were found to be loosely associated in fresh water, the compression of the electrical double layer and the adsorption of cations on kaolinite in sea water favored the formation of cross-linked network structures, exacerbating the entrainment of kaolinite in sea water (Zhang et al. 2015c).

The addition of pH modifiers can also alter the clay aggregation structures and therefore affect entrainment in flotation. Cruz et al. (2015b) reported that lime addition in flotation resulted in higher entrainment than soda ash, which was caused by the stronger kaolinite aggregates formed in the presence of lime. In another study, it was reported that the addition of gypsum to the ore–kaolinite mixture created aggregates with long strings further enhancing particle entrainment with more mass transported to the froth (Cruz et al. 2015c). Different from kaolinite, the addition of gypsum to the ore–bentonite mixture inhibited the formation of interconnected network structures, which led to lower viscosity

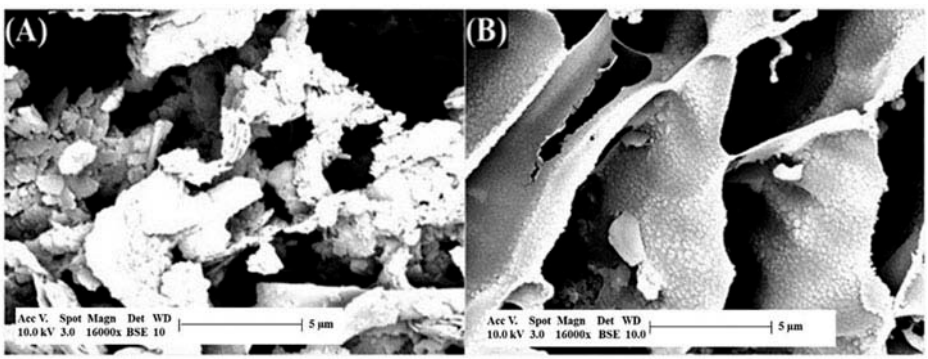

Figure 15. Cryo-SEM images of froth in the flotation of clean ore mixed with 15 wt.% kaolinite at a magnification of 16,000× in tap water (A) and sea water (B) (Zhang et al. 2015c).

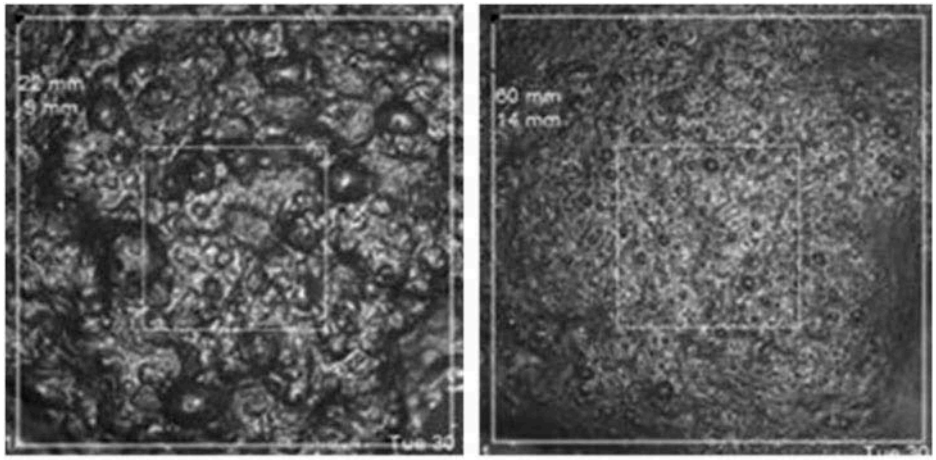

Figure 16. Froth image of the first concentrate in the flotation of Telfer clean ore in the absence and presence of 25% kaolinite (Wang et al. 2015b).

values with flotation behavior similar to that of mixtures with kaolinite. In this case, there was an improvement in recovery, but the grade decreased owing to entrainment. This finding supported the initial assumption that clay particle associations are the key to understanding flotation behavior.

The presence of fine clay particles in flotation can have significant effects on froth properties that also play a role in entrainment. Wang et al. (2015b) investigated the effect of kaolinite and bentonite on froth properties in copper–gold flotation. They found that the froth stability decreased with the addition of bentonite owing to the increase in pulp viscosity; however, as shown in Figure 16, the froth stability increased with an increase of kaolinite concentration together with the generation of smaller bubbles. It is known that stable froth with relatively low coalescence and small bubbles not only facilitates the recovery of attached particles but also promotes the recovery of gangue minerals by entrainment, which is the main reason for the reduced concentrate grade in the study by Wang and Peng (2013).

Furthermore, the formation of clay network structures may indirectly affect entrainment through the change in pulp rheology and froth rheology. As discussed in the previous section, clay minerals have the ability to significantly modify the pulp viscosity. Tests conducted by Kirjavainen (1992) using granular and flaky minerals at different slurry densities in the presence of frother alone showed that the recovery by entrainment was influenced by slurry viscosity. A viscous pulp will affect the degree of solids suspension in the pulp phase and also reduces the degree of sedimentation of particles owing to an increase in the drag force of the fluid (Shabalala et al. 2011). In addition, the presence of clay mineral aggregates in the froth may also elevate the viscosity of the froth that can affect entrainment. Shi and Zheng (2003) measured froth viscosity in industrial scale flotation tests and concluded that high froth viscosity led to an increase in froth residence time that decreased the water holdup in the froth phase and provided a longer time for water and entrained quartz to drain back from the froth to the pulp phase. Therefore, the high froth viscosity resulted in a decrease in the recovery of suspended quartz particles by entrainment and hence a lower grade in the concentrate.

Mitigation of negative effects of clay minerals on flotation

Removal of the coating of clay minerals

As discussed in previous section, the coating of clay minerals on valuable mineral/coal surfaces prohibits collector adsorption and decreases the hydrophobicity of valuable minerals/coals, leading to poor flotation performance. In order to mitigate the negative effects of clay coatings, the fine clay particles should be removed from the valuable mineral surfaces. Over the past decades, a number of methods for removing clay coating have been reported in the literature. A recent paper by Yu et al. (2017) has reviewed the methods to mitigate slime coatings. However, slime coating refers to the coating from all the fine particles rather than just clay minerals. Therefore, it is still essential to summarize the methods that have been reported to specifically mitigate the coating by clay minerals. Most of the methods fall into the following three categories: using mechanical forces to detach the clay minerals, applying dispersants to generate repulsive forces between clay minerals and valuable minerals, and using chemicals to selectively bind clay particles.

Application of physical methods in mitigating clay coatings

The main role of physical methods is to provide strong forces to overcome the attractive interaction force between the clay particles and valuable mineral particles. There are three technologies reported in the literature: high intensity agitation of pulps before flotation to separate clay minerals from the valuable mineral surfaces (Yu et al. 2017a, 2017b), the use of a desliming hydrocyclone that generates strong shear forces during the process (Oats et al. 2010), and ultrasonic treatment to detach the attached clay particles (Celik et al. 2002).

High intensity agitation was extensively practiced in the early 1930s and 1940s, and many researchers have demonstrated its benefits in mineral flotation with different mechanisms proposed, including improved collector dispersion and adsorption (Bulatovic and Salter 1989), creation of particle aggregates (shear flocculation) (Bulatovic and Salter 1989; Tabosa and Rubio 2010), and surface cleaning (Chen et al. 1999a, 1999b;

Yu et al. 2017a, 2017b). However, among all these studies, only the recent studies conducted by Yu et al. (2017a) and Yu et al. (2017b) investigated the ability of high intensity agitation to remove the coating of clay minerals. It was found that strong agitation during conditioning improved the flotation of coals in the presence of kaolinite. The authors proposed that the removal of clay particles that coated the coal surfaces was responsible for the improved coal flotation. In addition, it was found that agitation must reach a critical intensity in order to have a desliming effect. When agitation was below the critical intensity, the coating by clay minerals was increased, resulting in a decrease in coal combustible recovery.

Desliming hydrocyclones were also found beneficial in flotation of high-clay-content coals. Although the main role of desliming hydrocyclones in the plant is to classify the particles and separate the fines, it has been found that they can clean the mineral surfaces owing to the strong shear forces inside the hydrocyclone. In a study by Oats et al. (2010), desliming prior to flotation was found to be more effective than the addition of dispersants. However, this study did not provide direct evidence that the desliming cyclone actually removed the clay particle coatings on coal surfaces although the poor coal flotation performance before desliming was attributed to the slime coating. It is highly likely that other factors rather than coal surface cleaning may improve the flotation performance after desliming.

Celik et al. (1998) studied the effects of ultrasonic treatments on the flotation of boron minerals with heavy coatings of clay minerals on the surface. The results showed that while in the absence of ultrasonic treatment the recovery was only 5%, 60 s of sonication increased the recovery to more than 90%. The mechanism of this process was attributed to the applied ultrasonic treatment that helped detach clay particles from the surface. Although ultrasonic pretreatment showed promising benefits in the flotation of slime-coated minerals, the application of this technique in the plant is more challenging when compared to high intensity agitation and hydrocyclone desliming.

Application of chemicals in mitigating clay coatings

The slime coating of clay minerals on valuable minerals is mainly attributed to the attraction forces between the two types of minerals; therefore, chemical dispersants that can generate steric repulsion forces can be effective in reducing or completely mitigating the clay coating. Liu and Peng (2015) demonstrated that an anionic dispersant, lignosulfonate, improved the flotation of a problematic coal containing clay minerals. Mechanistic studies showed that the addition of lignosulfonate enhanced electrostatic repulsion between coal and clay particles by mitigating clay slime coatings from coal surfaces. However, lignosulfonate was found ineffective when coal flotation was conducted in saline water, because a low amount of lignosulfonate could not generate sufficient steric repulsion to remove clay particles from coal surfaces, while a high amount of lignosulfonate reduced coal surface hydrophobicity and depressed coal flotation even when clay coatings were removed from coal surfaces.

In addition to coal flotation, lignosulfonate was also found beneficial in the flotation of high-clay-content copper-gold ores (Seaman et al. 2012; Wei et al. 2013). Adsorption studies revealed that the dispersants demonstrated preferential adsorption onto the clay minerals, which suggests a scenario where the added dispersants prevented the coating of, in particular, the secondary copper sulfide, chalcocite (Seaman et al. 2012). A subsequent study conducted by Wei et al. (2013) determined that the effectiveness of lignosulfonate was sensitive to the contamination of mineral surfaces by grinding media. The application of forged steel grinding media produced a large amount of iron oxidation products that depressed copper and gold flotation and masked the role of the dispersant. Rheology tests were also conducted in this study to investigate whether the reduction in rheology by the dispersant was responsible for the improved flotation; however, no correlation between them was identified, which suggests that the main contributing factor to the increased recovery by dispersants was the removal of clay slime coating from the surface of valuable minerals.

As reviewed by Yu et al. (2017), there are many dispersants that have been shown to be effective in mitigating the coating of other slime particles, such as serpentine and quartz. However, they have not been evaluated in removing the clay coating. These chemicals can generally be classified into inorganic dispersants and polymeric dispersants. The most representative inorganic dispersants are $Na_4P_2O_7$ and Na_2SiO_3, which have been found effective in removing the coating of serpentine minerals from pentlandite (Edwards et al. 1980; Bremmell et al. 2005). Most of the polymeric dispersants are anionic polyelectrolytes and contain –COOH, $–SO_3H$, and $–OSO_3H$ groups. The most reported polymeric dispersant effective in mitigating slime coating is carboxymethyl cellulose (CMC), which has been widely used for dispersing the positively charged MgO-type gangue minerals in nickel sulfide flotation (Edwards et al. 1980; Wellham et al. 1992; Pietrobon et al. 1997; Bremmell et al. 2005; Peng and Seaman 2011).

In addition to dispersants, several studies have reported that a specially formulated low molecular weight polyaminoaldehyde polymer can reduce slime coatings by acting as a clay binder (Tao et al. 2007, 2010; Xu et al. 2012b). It has affinity for montmorillonite or kaolinite owing to their formulation and the chemical characteristics of clay minerals. The binder adsorption may result from a combination of mechanisms including electrostatic interactions, dipole–dipole interactions, chelation, and hydrogen bonding. Researchers have tested this chemical in coal flotation (Tao et al. 2007), phosphate flotation (Tao et al. 2010), and bitumen flotation (Xu et al. 2012b), and an improved flotation selectivity was observed in all the systems with an increase in recovery of valuable minerals and rejection of clay particles. The mechanism proposed is that this polymer functions as a slime depressant by agglomerating insoluble slimes to reduce their surface area and minimize their adsorption on valuable minerals and reducing the consumption of flotation reagents. However, this mechanism was not studied by the researchers and there was no direct evidence that the binder can remove the attached slime particles from the valuable mineral surface.

Reducing pulp viscosity

As discussed in previous section, the presence of clay minerals can significantly increase the pulp viscosity after reaching a critical concentration, which is generally detrimental to mineral flotation. The high viscosity of clay suspensions is related to the formation of network structures. Dispersants that can adsorb on clay mineral surfaces and produce repulsive forces to prevent the aggregation of particles have been found effective in reducing the slurry viscosity. In general, the dispersants effective for clay mineral suspensions can be classified into inorganic dispersants and polymer dispersants.

Application of inorganic dispersants to reduce pulp viscosity

Inorganic dispersants are normally sodium silicate and sodium polyphosphate. Papo et al. (2002) investigated the effect of sodium polyphosphate (PP) and tripolyphosphate (TPP) as dispersing agents on the rheological behavior of kaolin suspensions. The results indicated that increasing the amount of both dispersants in a pure kaolin suspension resulted in a gradual decay in viscosity. A further addition of dispersant above the adsorption saturation limit led to an excess concentration in the solution that caused destabilization, flocculation, and an increase in viscosity owing to suspension coagulation. The study also revealed that a higher polyphosphate addition caused shear-thickening behavior. This was explained in terms of PP chain interactions where the non-adsorbed segments of PP molecules extending toward the water solution interact with each other. Goh et al. (2011) studied the effects of polyphosphate addition on yield stress–pH behavior of a bentonite slurry. They found that polyphosphate reduced the strength of the attractive force between clay particles as indicated by the much smaller yield stress, causing the slurry to become completely dispersed at pH greater than 6. At lower pH values, strong attractive interaction between the negative edge and positive face and high particle density led to the formation of a strong house-of-cards structure. The adsorbed polyphosphate formed an electrosteric barrier at the particle edge weakening the house-of-cards structure. At pH above 6, the phosphate additives located at the junction of the edge-face could act as a steric layer keeping the F(-)F(-)-interacting particles further apart and reducing the strength of the attractive forces. When the F–F separation was considerably far apart, the cation-mediated F–F attraction could become considerably weak to form a network structure. In general, these studies support the hypothesis that the addition of inorganic dispersants is able to reduce the viscosity of clay suspensions; however, there is no study that investigates how these dispersants can benefit flotation.

In addition to common inorganic dispersants, the presence of other salt ions (e.g., cations Ca^{2+}, Na^{+}, Mg^{2+} and anions Cl^{-}, SO_4^{2-}, CO_3^{2-}) has been found to be effective in reducing the high pulp viscosity of high-clay-content suspensions (Heller and Keren 2001; Lagaly and Ziesmer 2003; Suzuki et al. 2005). The effects of these ions on pulp rheology in flotation and on flotation performance have been reviewed previously (Cruz et al. 2013, 2015a, 2015b, 2015c; Zhang et al. 2015b; Wang et al. 2016). These studies have confirmed that pulp viscosity can be reduced by the addition of some ions, which then improves the flotation performance.

Application of polymer dispersants to reduce pulp viscosity

Polymer adsorption on clay minerals happens at both the basal surface and edge surface of clay minerals, and modifies the strength of the interparticle forces, resulting in a network with different structures. There are mainly two principal mechanisms for the stabilization of particle dispersions: electrostatic stabilization and steric stabilization. The influence of a negatively charged grafted block copolymer (CTP) onto the threshold stress value of illite and kaolinite dispersions was investigated in a strongly alkaline environment by Konan et al. (2008). It was found that as the amount of CTP into the dispersion increased, the threshold stress values decreased for both clay minerals, with a more pronounced effect for kaolinite than for illite. It was also confirmed that steric stabilization was the main dispersion mechanism (Konan et al. 2008).

Zhang et al. (2012) investigated the interactions between kaolinite clay particles and a comb-type polymer, polycarboxylate ether (PCE) in acidic and alkaline media. They found that at pH 3.4, kaolinite particles could self-aggregate through the electrostatic attraction between negatively charged clay basal planes and positively charged edge surfaces, and a low dosage of PCE brought small aggregates together through the hydrogen bonding between PCE side chains and clay surfaces. With increasing the dosage of PCE, PCE molecules fully covered the self-aggregated clay particles and induced strong steric repulsion between these aggregates. At pH 8.3 at which the kaolinite suspension was well dispersed, a low dosage of PCE was able to bind particles together and form strong network through hydrogen bonding between PCE molecules and particle surfaces. At a high PCE dosage, the PCE molecules fully covered the clay particle surfaces, inducing strong steric repulsive forces between the particles.

Biopolymers, such as lignosulfonate-based polymers, have been found effective as clay dispersants and improve flotation. The studies by Seaman et al. (2012) and Wei et al. (2013) all confirmed that lignosulfonate dispersants can improve the flotation performance. However, the mechanistic studies focused on the mitigation of clay slime coating on valuable mineral surfaces. The improved flotation may also partly result from the reduction of slurry viscosity.

Reducing entrainment of clay minerals

As reviewed in previous section, the main factor contributing to the high entrainment of clay minerals in flotation is their fine particle sizes and loose structures formed. Aggregating clay minerals to form dense structures by the application of polymers is a potential way to reduce the entrainment. A recent study by Liu and Peng (2014) has proved that the addition of high molecular weight polyethylene oxide (PEO) significantly reduced the entrainment of kaolinite in flotation by aggregating kaolinite particles in flotation. The aggregation behavior of kaolinite Q38 particles in the absence and presence of PEO and its

effect on the entrainment of kaolinite Q38 were studied by the in situ measurement of flocs and the size of enlarged particles by inserting a Particle Vision Measurement (PVM) instrument and Focused Beam Reflectance Measurement (FBRM) instrument in the flotation cell. The system setup and an example of measurement results are shown in Figure 17. It is interesting to note that PEO did flocculate kaolinite Q38 particles and enlarge their sizes in flotation despite high agitation. In addition, it was found that the effect of PEO on the reduction of entrainment of kaolinite Q38 in flotation using saline water was less pronounced owing to the formation of less compact flocs and enhanced froth stability.

Except the study by Liu and Peng (2014), there is no study on the application of polymeric flocculants to reduce the entrainment of clay minerals in flotation. Some previous studies have however tested a similar approach in other mineral systems. Liu et al. (2006) showed that the entrainment of iron oxide in flotation was reduced by forming aggregates of iron oxide particles using high molecular weight CMC or corn starch to flocculate them. Gong et al. (2010) demonstrated that PEO with a molecular weight successfully reduced quartz entrainment in the flotation of a copper–gold ore. Gong et al. (2010) also used a Photometric Dispersion Analyzer (PDA) to investigate the flocculation/dispersion behavior of quartz, chalcopyrite, and their mixtures in the presence of PEO. It was found that PEO selectively adsorbed on quartz particles, leading to the formation of aggregates. The quartz flocs that were sufficiently large to overcome the fluid drag were therefore less prone to recovery by entrainment. In general, these studies indicate that the application of polymeric flocculants is effective in reducing the entrainment of gangue minerals.

In addition to the high molecular weight flocculant, a low molecular weight polyaminoaldehyde polymer has been found to be effective in improving the flotation selectivity in high-clay-content systems by acting as clay binder to agglomerate clay particles (Tao et al. 2007, 2010; Xu et al. 2012b). Although the mechanisms proposed by the researchers were the removal of the slime coating of fine clays from particles/bubbles and the reduction of reagent consumption owing to the reduced total surface area upon particle agglomeration, it is highly likely that this chemical may also reduce clay entrainment through enlarging the particle size by means of aggregation.

Future research

The above review of the literature has clearly demonstrated the current knowledge of the various effects of clay minerals on flotation and the approaches developed to mitigate their negative effects. However, there still exist many research gaps that should be addressed before the effects of clay minerals on flotation can be fully understood. In addition, most of the developed approaches to mitigate the negative effects are still not applicable. Therefore, the following research directions are suggested to fill these gaps.

(1) *Isolating the different negative effects of clay minerals on flotation.*

Based on the reviewed literature, clay minerals have a deleterious effect on mineral flotation through different mechanisms, including clay coating, increased pulp viscosity, and entrainment. In a real mineral flotation plant, the negative effects of clay minerals on flotation can be caused by one of the above mechanisms or a combination of different mechanisms. For example, depressed copper flotation in the presence of clay minerals can be caused by clay coating or increased rheology or a combination of both. It is important to identify the main mechanisms involved in order to develop suitable approaches to mitigate their negative effects on flotation.

(2) *More robust and in situ characterization of clay slime coatings in real flotation systems.*

A review of the literature shows that many studies claim that the clay coating is the main contributing factor to the deterioration of flotation performance without a direct characterization of the clay coating. This can lead to incorrect conclusions and mechanisms being proposed. This situation is mainly related to the lack of available techniques to characterize clay coatings under flotation conditions. To date, the main characterization methods used in the literature include Scanning electron microscopy (SEM), AFM, and some electrokinetic measurements that are difficult to characterize the clay coating in a real flotation system. The development of more robust techniques will have significant benefits to identification of mechanisms and problem solving.

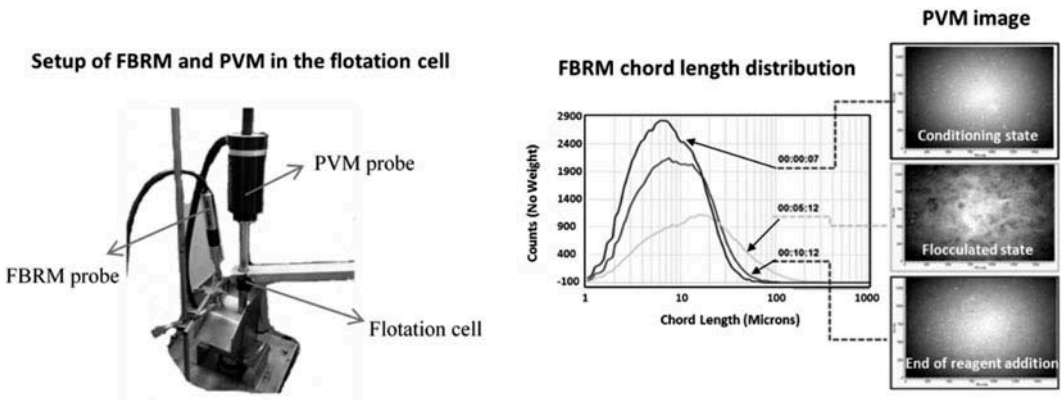

Figure 17. The set-up of FBRM and PVM measurements in the flotation cell and the PVM image of kaolinite Q38 particles with addition of 100 g/t PEO and its synchronized FBRM chord length distributions measured at different time in saline water (Adapted from Liu and Peng (2014)).

(3) *Effects of mineral/coal surface species on clay coatings.*

During mining and mineral processing, mineral surfaces can be oxidized to different degrees and/or contaminated by different species. Recent studies at The University of Queensland have shown that the oxidation of chalcocite may promote clay coating (Peng and Zhao 2011; Zhao and Peng 2012). It is highly likely that other minerals or coals also display similar behavior. In addition, when conducting studies with real ores, laboratory work should be conducted under conditions similar to plant conditions to ensure the generation of similar surface species to those in the plant.

(4) *In situ characterization of clay network structures*

Based on the review, clay network structures play critical roles in both pulp rheology and entrainment. However, there is no technique that can be applied in situ to characterize the clay network structures in a slurry. The main technique used in previous studies at The University of Queensland is Cryo-SEM. Although Cyro-SEM can preserve the clay network structures, it requires complicated sample preparation and is difficult to access by the industry. A development of in situ techniques to characterize the clay network structures will have significant benefits to further understanding the clay network structures in real flotation systems.

(5) *Development of effective reagents for removing clay coatings in high salinity water*

A review of the literature shows that the application of dispersants is an effective approach in the removal of the deleterious clay coatings. However, it has been found that an anionic dispersant that is effective in flotation with fresh water did not work in flotation with saline water (Liu and Peng 2015). Considering the widespread use of saline water or sea water in flotation, it is important to investigate the effects of water salinity on the dispersing effect of chemicals and develop chemicals that are effective in saline water.

(6) *Application of dispersants to reduce pulp viscosity and improve flotation*

There are various dispersants, both inorganic salts and polymers available to reduce the pulp viscosity. However, the research on applying these dispersants in flotation systems is limited. The high pulp viscosity imparted by clay minerals can significantly depress mineral flotation. The identification of suitable dispersants that can reduce viscosity without negative effects on flotation will have a high potential to be applied to improve the flotation of high-clay-content ores.

(7) *Modification of clay network structures to reduce the entrainment of clay minerals*

High entrainment of clay minerals is a significant challenge in the flotation of clayey ores. A previous study at The University of Queensland shows that applying polymers to flocculate clay minerals to form dense aggregation structures is a potential way to reduce entrainment (Liu and Peng 2014). However, further studies are required to comprehensively investigate the change of network structures after the application of polymers, the relationship between the different clay network structures and the degree of entrainment, as well as the effects of polymers on the floatability of valuable minerals. In addition, the identification of more effective chemicals to achieve optimized clay network structures is necessary.

Conclusions

This paper presents a critical review of the effects of clay minerals on flotation. Clay minerals commonly occurring in ore deposits are classified into three groups: kaolin group, smectite group, and illite group. Although all clay minerals consist of tetrahedral (T) sheets and octahedral (O) sheets, different clay minerals have different layer structures and bonding forces that lead to different properties. The other important property of clay minerals is their surface charge that determines the interactions of clay minerals between each other and with valuable minerals. According to zeta-potential measurements, clay minerals are typically negative charged in the flotation context; however, their edges can carry positive charges depending on the solution chemistry, which can play an important role in clay coatings and clay particle interactions.

The presence of clay minerals has various detrimental effects on flotation. The first negative effect is the coating of clay minerals on valuable mineral surfaces that prevents the adsorption of collectors and reduces the particle hydrophobicity, resulting in a decreased flotation recovery. The most widely accepted mechanism for slime coating is the electrostatic attraction between clay minerals and valuable minerals. Other mechanisms including van der Waals attraction and hetero-coagulation by the ions present in a slurry have been reported in the literature. The degree of clay coating in a flotation system is determined by many factors such as the structure of clay minerals, the surface properties of valuable minerals, the pH of the slurry, and the presence of electrolytes in the system.

The other negative effect of clay minerals is through the formation of network structures. First, the network structures can significantly modify the pulp viscosity and lead to decreased flotation recovery. The significance of rheology modification by clay minerals is mainly determined by the type and the crystalline degree of clay minerals that lead to the formation of different network structures. In addition, the change of pH and the presence of electrolytes in a slurry can significantly modify the clay aggregation structures and in turn affect pulp viscosity. Besides the modification of pulp rheology, the formation of network structures also affects the degree of entrainment of clay minerals. Light and loose aggregation structures tend to be more easily entrained into flotation concentrates. Studies also suggest that clay minerals may affect the entrainment through the change of froth properties and pulp rheology.

Various approaches to mitigate the negative effects of clay minerals in flotation have been reported in literature. To remove the clay coating from the valuable mineral surface, both physical methods and chemical methods have been reported. The

physical methods include the application of high intensity conditioning, desliming cyclones, and ultrasonic treatments; whereas, the effective chemicals include inorganic dispersants, polymeric dispersants, and a specially designed clay binder. To reduce the pulp viscosity, the main method reported is the application of dispersants including inorganic dispersants and polymeric dispersants. Studies on reducing the entrainment of clay minerals are however limited. One potential method reported to reduce the entrainment of clay minerals is the aggregation of fine clay particles to form larger and denser aggregates.

Based on the review of the literature, future research directions are recommended for a more complete understanding of mechanisms including further studies on how to isolate the different negative effects of clay minerals on flotation, more robust and in situ characterization of clay slime coatings in real flotation systems, investigating the effects of mineral/coal surface species on clay coatings, and developing techniques for in situ characterization of clay network structures. Development of more effective mitigating approaches is also recommended, including developments of effective reagents for removing clay coatings in high salinity water, application of dispersants to reduce pulp viscosity and improve flotation, and the modification of clay network structures to reduce the entrainment of clay minerals.

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